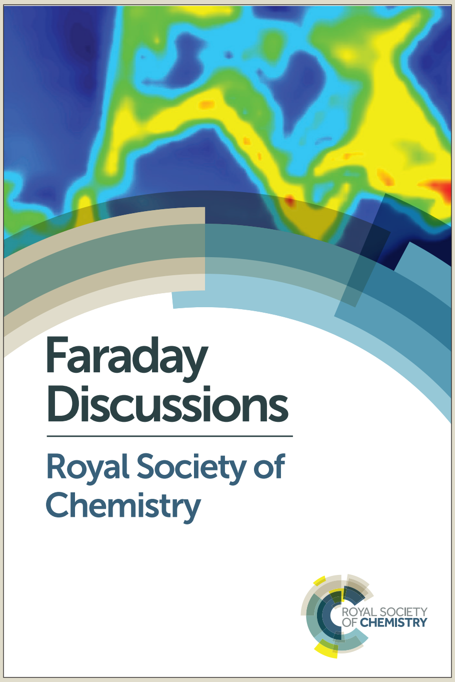
Faraday Discussions

Accepted Manuscript

This manuscript will be presented and discussed at a forthcoming Faraday Discussion meeting. All delegates can contribute to the discussion which will be included in the final volume.

Register now to attend! Full details of all upcoming meetings: http://rsc.li/fd-upcoming-meetings



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY
OF CHEMISTRY

www.rsc.org/faraday_d

Faraday Discussions: CORROSION CHEMISTRY

ARTICLE

www.rsc.org/

CORROSION Chemistry Closing Comments: *Opportunities in Corrosion Science Facilitated by Operando Experimental Characterization Combined with Multi-Scale Computational Modelling*

Received 00th January 20xx, Accepted 00th January 20xx (FD-ART-05-2015-000075)

DOI: 10.1039/x0xx00000x

John R. Scully[a]

Recent advances in characterization tools, computational capabilities, and theories have created opportunities for advancement in understanding of solid/fluid interfaces at the nanoscale in corroding metallic systems. The Faraday Discussion on Corrosion Chemistry in 2015 highlighted some of the current needs, gaps and opportunities in corrosion science. Themes were organized into several hierarchal categories that provide an organizational framework for corrosion. Opportunities to develop fundamental physical and chemical data which will enable further progress in thermodynamic and kinetic modelling of corrosion were discussed. These will enable new and better understandings of unit processes that govern corrosion at the nanoscale. Additional topics discussed included scales, films and oxides, fluid-surface and molecular-surface interactions, selected topics in corrosion science and engineering as well as corrosion control. Corrosion science and engineering topics included complex alloy dissolution, local corrosion, and modelling of specific corrosion processes that are made up of collections of temporally and spatially varying unit processes such as oxidation, ion transport, and competitive adsorption. Corrosion control and mitigation topics covered some new insights on coatings and inhibitors. Further advances in *operando* or *in-situ* experimental characterization strategies at the nanoscale combined with computational modelling will enhance progress in the field, especially if coupling across length and time scales can be achieved incorporating the various phenomena encountered in corrosion. Readers are encouraged to not only use this *ad hoc* organizational scheme to guide their immersion into the current opportunities in corrosion chemistry, but also to find value in the information presented in their own ways.

1 Introduction

Recently, there has been substantial progress in the development of experimental and theoretical methods for probing metals, scale or passive films, and solid/fluid interfaces at the nanoscale [1]. The field of corrosion science, focusing on degradation of metallic materials exposed to liquids and gases, can capitalize on these recent advances with the ultimate goal of relating nanoscale understanding to engineering behaviour. The technological needs and challenges associated with corrosion are particularly acute as our highly engineered civilization moves towards nanoscale devices dependent on the stability of every atom, the use of engineered materials in increasingly complex and harsh environments, increased reliability over the long term epitomized by very diverse challenges such as health care appliance reliability and engineered nuclear waste packages, rapid material replacement and insertion, and the reinvention of the last century's disposability materials-based society with a more sustainable one [1]. The aim of this Faraday Discussion was to bring together experimentalists and theoreticians concerned with understanding interfacial chemical processes at the nanoscale relevant to corrosion and its control [1].

CORROSION CHEMISTRY conducted from April 13-15, 2015 provided a snap shot of the current status of the corrosion field touching upon many of the issues mentioned above. Given the task of reflecting on the many papers, posters, and discussion comments, it is important to

---

[a] Center for Electrochemical Science and Engineering, Department of Materials Science and Engineering, SEAS, University of Virginia, Charlottesville VA USA 22904: email: jrs8d@virginia.edu; TEL +1-434-982-5786; Fax: +1-434-982-5799

DOI: 10.1039/x0xx00000x

note that no closing lecture or written summary could give justice to the papers, posters and many valuable points made in the discussions. The organizational scheme adapted herein represents “my take” on the overall themes of this diverse and multi-disciplinary field. Other organizational structures may serve as well or better. Each paper and poster contained many facets illuminating corrosion advancements and remaining issues as well as touching upon a number of the themes listed above. To borrow an example from the internet, web browsers learn, adapt and then reposition the presentation of topics based on the visitation records and popularity of a particular site or topic. In a similar fashion, the enduring scientific value of each paper and what aspects are seen as the most beneficial to the field will be voted upon over time by the corrosion community and cannot be determined *a’ priori* by a closing lecturer. My primary hope is that the closing comments made below will point readers towards papers that might not have otherwise been considered for deep immersion and consideration.

This closing comment is organized by the themes above as depicted in Figure 1; these include underlying fundamentals, unit processes and phenomena, and corrosion science and engineering. Figure 1 illustrates the hierarchal nature of corrosion. Fundamentals include thermodynamic and kinetic data of value towards corrosion computations. Unit processes included films and scales, solid-fluid interfaces and molecular interactions with surfaces. Corrosion science and engineering included modelling of defined aspects of corrosion processes, localized corrosion and complex alloy dissolution, as well as corrosion control. Each paper presented contained several facets and reasonably fell into several of the areas of this hierarchal scheme. Moreover, corrosion is an inherently multi-scale process where nanoscale chemical, physical and electrical events govern unit processes which in turn assemble to regulate or control larger-scale corrosion processes (Figure 2). Fundamental laws of thermodynamics of scales and bulk materials, interfaces and electrolytes are critical inputs to crucial unit processes in corrosion such as transport, adsorption, redox reaction, and precipitation. In turn, these unit processes operate in concert to regulate the events taking place during corrosion as well as the engineering consequences. These processes may interact at the nanometre, micrometre or millimetre scales to regulate and control engineering scale corrosion processes. Often corrosion events themselves may occur in sequence or in series. For instance, coating or inhibitor film breakdown may be followed by local corrosion or dealloying which is followed by stress corrosion or corrosion fatigue. Such an assemblage requires the linking of corrosion stages; each containing its own unit processes. Only at this point can corrosion control be considered; ideally guided by nanoscale understanding of all the contributing processes.

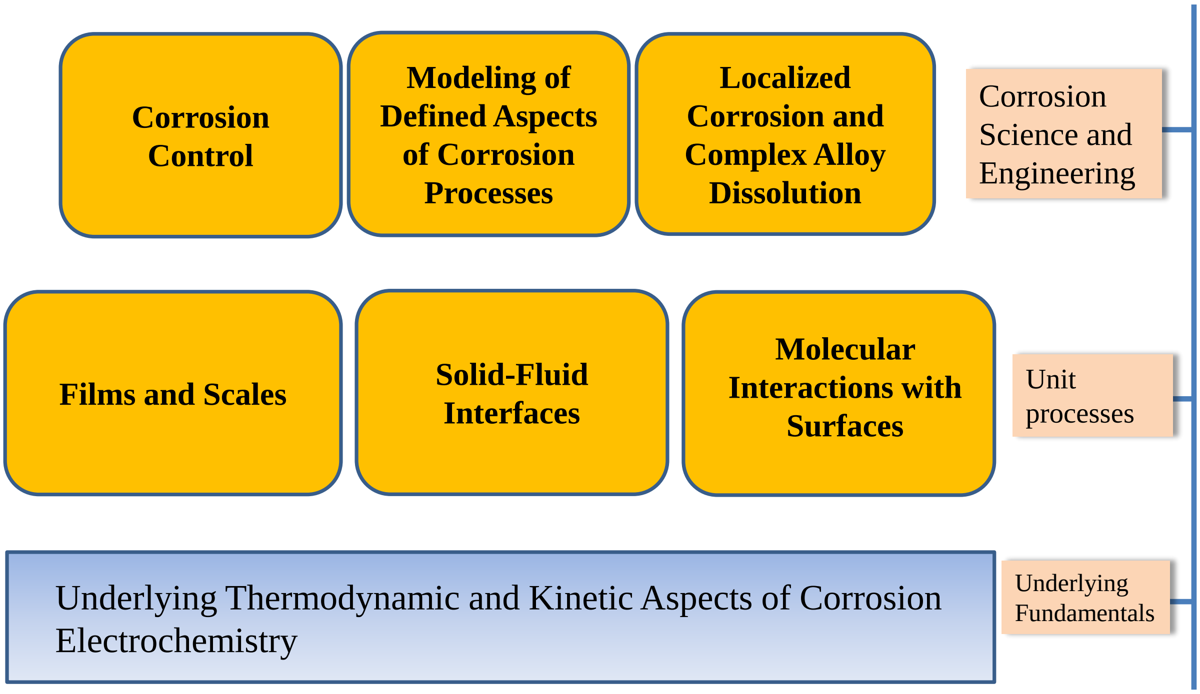


Figure 1. Corrosion chemistry research areas discussed at the RSC Faraday Discussion on Corrosion Chemistry in April 2015. Each paper presented could be organized into one or more of these areas. The underlying fundamentals inform the various unit processes which together form sets of coupled processes that contribute to the understanding of multi-disciplinary corrosion science and engineering problems addressed by the corrosion field.

Readers are encouraged to “find” their own value in each paper and the ensuing discussion in whatever manner is the most valuable to their research efforts. This closing comment, drawing inspiration from the insightful papers presented, concludes with some suggestions regarding how corrosion science might be advanced. Please enjoy this overview as much as I enjoyed the conference.

2 Fundamentals

Given the multi-disciplinary nature of the corrosion field, scientific progress in phase field and phase stability studies as well as kinetic models of phase formation and growth rely upon fundamental chemical, structural, physical and electronic information. This information is a necessary input to model the thermodynamics and kinetics of individual unit processes, which when combined attempt to explain various corrosion phenomena. Therefore, fundamental thermodynamic and kinetic parameters must continue to be defined, calculated, reported and perhaps further refined after experimental scrutiny in order to enable accurate modelling. Design of safe windows of operation, computational corrosion materials design, as well as corrosion control strategies will also rely on such information. Phase field construction by computational modelling requires fundamental thermodynamic information as inputs. Papers presented demonstrated that it is possible to develop multiple levels of understanding of phase fields beyond the classical potential-pH regions of oxide stability, and metal dissolution. For instance, it is now possible to compute the type of oxide defects present in a phase field where a specific oxide is stable, as well as equilibrium concentrations of each type of defect considered [2]. The effects of defects on the boundaries of the phase fields and E-pH diagrams, effects of applied stress, surface adsorption and other factors can now be computed using first principles methods as a function of external variables and will likely add further insights into corrosion[3-8].

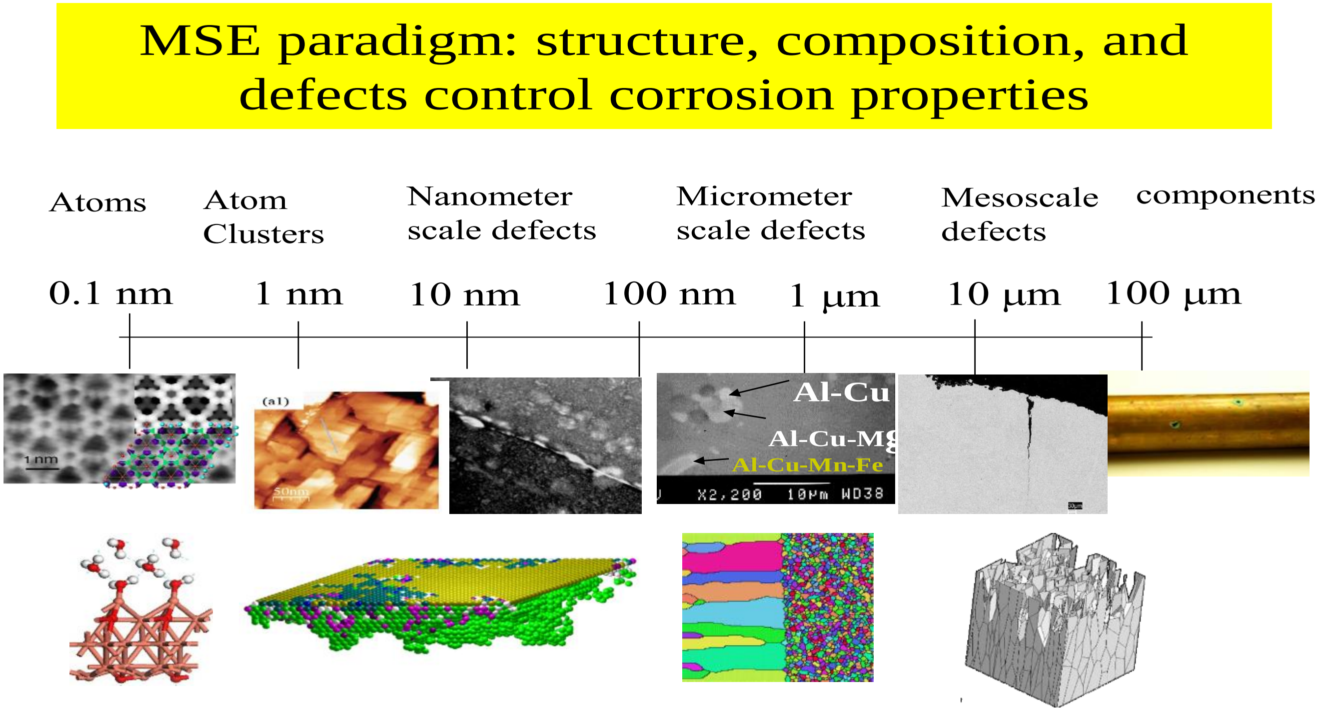


Figure 2. Hierarchy of the multi-scale corrosion problem starting at the atomic scale and transitioning to the micrometre scale and above. Critical processes at different length scales may factor in to regulate engineering scale corrosion of the copper pipe observed at the far right. It is also noted that the various model length scales from first principles, Monte Carlo, and continuum scale may or may not match the physical or microstructural scale. (Reprinted with Permission, National Academy Press).

Many oxide covered metal interfaces that control corrosion are either monolithic semiconductors or p-n semiconductor junctions in conformal layers. Noteworthy was a paper connecting the field of semi-conductor defect physics and electrochemical concepts [2]. The most thermodynamically stable point defects as a function of electron chemical potential and proton activity or potential and pH were predicted for a given oxide. In the future this could be extended to other compounds involved in corrosion scales such as hydroxides, carbonates, and phosphates. This paper bridges the gap between semiconductor "physics" and corrosion. Understanding the type and concentration of the most stable defect type in oxides is essential to and sheds light on the effects of electric field and chemical potential driven transport and growth processes in passive films. It also suggests which point defects might be of interest to control transport and ultimately oxide growth. Another bridge head was developed by linking corrosion relevant oxide properties with mineral scale expertise at the nanoscale [9]. Further progress can enlighten understanding of how defect sequestration, oxide dopants or other mitigation strategies might or might not be advantageous towards corrosion [2]. As pointed out, there is cross-cutting interest in geochemistry, colloid science, catalysis, nanotechnology, soil and clay chemistry and corrosion regarding the properties of oxidized surfaces where information is sought in multiple dimensions such as surface structure and macroscopic surface charge [9]. In the specific example presented, the atomic and electronic structures of aged and fresh hematite were considered over exposure time and related to the isoelectric point of the oxide surface over a range of pH. A working framework of the structure, composition and local electronic density of states of valence (conduction) band electrons was constructed. This detailed understanding has applicability to all oxide covered metals and would provide better ability to elucidate how the scaled surface might interact with the ionic electrolyte and adsorbing molecular species as well as polar molecules during corrosion. A third advance was to consider phase stability and oxygen adsorption in the presence of compressive and tensile stress [4]. It was shown that the oxygen adsorption energy changed with tensile and compressive strain. Such data shows that the strain induced by oxygen adsorption can be offset by external stress and that under potential surface oxidation may be affected by tensile strain.

In total these papers shed light on how greater basic insight into fundamental aspects of surfaces, interfaces, and phases enabled by modelling will move the field of corrosion science forward [2, 4, 9].

3 Critical Unit Processes in Corrosion

There are many unit processes at interfaces and across films that govern or mediate corrosion. Unit processes across films and interfaces discussed included film and scale formation, and growth, as well as molecular interactions and reactions at surfaces/solid-fluid interfaces. All of these play a role to control or otherwise mediate electrochemical corrosion reactions including anodic and cathodic half-cell reactions. While these individual processes do not themselves describe everything about a corrosion process, they are critical unit processes. For instance, ionic transports across a scale or how a scale controls an electrochemical reaction at the metal/scale interface are of paramount importance in corrosion. Progress must be made in understanding these individual processes in order to move the field forward.

3.1 Films and Scales

An enduring theme in corrosion is the need to understand oxides, films, and scales. Corrosion in aqueous solutions, upon atmospheric exposure and at high temperature is often mediated and controlled not only by conformal nanometre scale oxides, but by thick scales and films adherent to metallic substrates. Corrosion scales and passive films can both significantly affect corrosion (e.g., a passive film can reduce corrosion to a negligible rate).[1]. Experimental/theoretical studies concerning both engineering and model (e.g., single crystal) substrates were presented. Relationships between the composition-structure-chemistry-corrosion resistance of scales and films were addressed, together with insight into processes governing their initiation and growth, including the impact of environmental conditions [1].

The identity and structure of these layers is dictated by the underlying materials, the solution, and the molecular and colloidal species in the solution and/or all of these. Therefore, the exact nature of the protective scale is hard to predict *a' priori*. Crucial to progress in the corrosion field is the need to obtain *in-situ or operando* chemical, structural and mechanical information about of these films and scales. Particularly exciting was progress in understanding the chemical, oxidation state, and chemical environment of these layers and films accessed only recently by X-ray photoelectron spectroscopy (XPS) through thin water layers. The chemical environment and oxidation behaviour of metal oxides in dry, humid, and wet conditions was investigated [10]. This information was combined with electrochemical treatments to produce different oxides interrogated by *operando* XPS [10]. Continuing on the theme of examination of scales and films in situ was work examining the temporal stages of thick film formation on iron in CO_2 under electrochemical control. The global corrosion status could be compared to operando observations on scaling [11]. The value of characterizing the colloidal properties of the solution, the amorphous gel formed on the surface followed by reorganization as a crystalline scale of siderite all while acquiring global electrochemical corrosion data was evident. Small and wide angle x-ray scattering experiments examined the iron CO_2 interface almost simultaneously for an unprecedented view of the events during scaling. It was found that small amounts of dissolved Cr critically effect scale formation. Lastly, a multi-faceted investigation into the effect of Mo on passivation in Fe-Cr-Ni and Fe-Cr-Ni-Mo alloys revealed the enormous value in applying several in-situ and ex-situ techniques simultaneously to unravel the long standing need to understand the beneficial role of major, trace and minor alloying elements on passivity and passivity breakdown [12]. Single crystal (111) surfaces were investigated. Ex-situ x-ray photoelectron spectroscopy (XPS) and time of flight secondary ion mass spectrometry (ToF-SIMS) data were compared and contrasted [12]. Atomic scale morphological information was acquired in concert using in-situ STM investigation of passivating terraces and ledges. To this end, the chemical, oxidation state, molecular and morphological behaviour of an electrochemically passivated Fe-Ni-Cr passivated surface was directly compared to the same alloy containing Mo. Several roles of Mo were identified and the fate of alloying elements at the metal/oxide, oxide layer, and within terrace sites was elucidated [12].

With the age of environmental microscopes for *operando* interrogation, progress in this area of corrosion science is expected to produce unprecedented new findings, with some perhaps being transformational.

3.2 Solid Liquid Interfaces and Interactions of Molecules at Surfaces

In the corrosion field, information is sought about the underlying substrates, each interface, each film, scale, or layer, each synthetic coating or pre-treatment, as well as the interaction of water and the electrolyte both near the electrode surface at both double layer length scales and further away in the bulk of solution. Often corrosion research has been piecemeal where only one or two of these aspects are characterized often *ex-situ* or upon air transfers. Challenges in corrosion include the need for real time *in-situ* spatial ~~as well as lateral~~ characterization, depth profiling as well as the need for multi-channel information or “corrosion in 4-D.”

New nanoscale understandings of the structure and fundamental chemical processes (e.g. ion adsorption) at solid/fluid interfaces were discussed. Particular attention was given to solid/aqueous solution interface, as they are of central importance to corrosion [1]. Ideally a layer-by-layer approach enables simultaneous characterization of each layer involved in a corroding interface [1]. Often, there is a metal conductor, semi-conductor oxide film, an amorphous highly porous outer film, and a colloidal solution within the overlying ionic conducting phase. It is clear that much is to be learned about the double layer, the structure of water near various oxide and metal interfaces as a function of potential, as well as the nature of non-traditional scales that may fall somewhere in between compact oxides and colloidal solutions near such interfaces.

The concept of obtaining in-situ information at the oxide/liquid buried interface was exemplified in the study of radiolysis driven dissolution and the UO_2/water interface. Intense X-ray beams were utilized for in-situ X-ray reflectivity and high angle diffraction (XRD). Information on layer thickness and thus rate of dissolution, roughening and electron density was obtained [13]. Moreover, the crystalline nature of the layers and dislocation defects could be examined. A layered UO_2/UO_x and a UO_x/water interface model was constructed and new nanoscale detail was revealed, possibly altering the understanding of current models addressing long term storage of spent nuclear fuel. The study of CO_2 corrosion also interrogated both the scale and the colloidal solution properties of the solution above the scale, concurrently, while collecting electrochemical information. Together these studies provide an unprecedented view of how a corroding interface behaves and responds to various environmental factors during corrosion [11].

The interactions of special molecules at aqueous interfaces were also explored. In corrosion, inhibitor molecules and certain proteins can limit corrosion. In contrast, film disrupting ions can replace metal cations in oxides or otherwise damage oxides and reacting species such as thiosulfate can react on corroding surfaces leading to detrimental reduced species such as sulphur. Sulphur can in turn catalyse dissolution of certain metals (e.g. nickel) [14]. One example of an interacting naturally occurring molecule is bovine serum albumin (BSA) and its interactions with pure Mg and Fe during corrosion is of great interest in *in vivo* studies such as those related to implant materials in humans. BSA has a strong interacting effect with Mg which leads to corrosion inhibition whereas selected accelerated corrosion is induced by interactions with Fe [15]. Moreover there was complex time dependence with this interaction. Favoured BSA adsorption and subsequent corrosion inhibition occurred in the case of Mg. This was traced to electrostatic interactions between the protein and the metal oxide which depended on the bond strength between metal cations and protein molecules [15].

Chemical inhibitors are a key area of need for corrosion protection but also a fertile ground for rapid science advance. The first step concerns the interactions of molecules with surfaces while the second should consider the broader scope of the processes that conspire to regulate corrosion [16-18]. Computational studies with focus on surface interaction and. adsorption phenomena have blossomed, perhaps led by the catalysis field. An ever increasing number of synthesized molecules and natural organic species may have potential as corrosion inhibitors. A major issue in the corrosion field is how to sort, categorize, and otherwise “screen” molecules for good replacement inhibitors which are at the same time more chemically friendly to the environment. Ab Initio studies (mainly using Density Function Theory or DFT) have come of age and can begin to address the interaction of molecules with surfaces. In the FD it was pointed out that this task is much more difficult in the field of corrosion compared to reaction catalysis where relatively straight forward attributes of molecule-solid catalyst interactions may shed light on the qualities of the most favourable catalysts. The corrosion challenge is somewhat more complex partly due to the number of important steps involved in the overall rate determining process and the number of physical processes conspiring to regulate corrosion rate. Moreover, the complexity of many corrosion environments is substantial; with environments often containing ionic, molecular, polymeric, and colloidal species in one mixed environment [18].

A common starting point in this issue is adsorption which is generally viewed as a key process by which corrosion inhibiting molecules improve corrosion resistance. The issue of bond strength of deprotonated and protonated inhibitor molecules in different orientations was directly addressed in Ab Initio studies of benzotriazole or $C_6H_5N_3$, hereafter referred to as BTAH. This is a well-known corrosion inhibitor of copper [16, 17]. It was shown that the inhibitor molecule was able to bond to both oxide covered and oxide free surfaces. Moreover, BTAH may passivate under-coordinated copper sites that are “plausible sites for Cu oxidation”. Organic metal complexes are also formed suggesting that “at risk” copper ad-atoms could be stabilized by inhibiting molecules [17]. The good qualities in an inhibiting molecule and the bad qualities were subsequently debated. No single metric accessed by Ab Initio methods seem to readily describe this; the consensus was that a combination of inhibitor qualities is needed and a good starting place is to understand adsorption. A soluble inhibitor molecule–metal complex was regarded as bad; strong adsorption could be good if electron donating events could be reduced by the presence of an absorbed species; for instance, metal oxidation and Cl^- adsorption [17]. Indeed, Cl^- and water adsorption energies were compared to the BTAH and BTA^- adsorption energies on copper crystals of different orientation and fairly strong competitive adsorption was suggested. Subtleties such as the how the BTAH and BTA^- are oriented with respect to the surface plane were shown to be very important with strong chemi-sorption via the azole moiety with coverage, protonation, and van der Waals forces all playing a role. Coverage changes the molecule arrangement ranging from flat lying towards end–to-surface configurations with inhibitor concentration which enabled close packing of BTAH. However, the attributes of a bad inhibitor in terms of a calculated metric were not entirely clear. Moreover, competitive adsorption needs to be considered in the complex electrolyte. Studies to date consider the bond strength of Cl^- versus the bond strengths of BTAH or BTA^- in isolation from each other and in a vacuum without lateral interactions. Studies at the next level should include inhibitor, competitive adsorbing ion and water molecules at the interface. Moreover, these bond strength arguments are weakened by limited insights regarding how the dissolution rate of first, second and third nearest neighbour adsorption sites might be affected by proximate adsorption. This has been considered elsewhere [7]. The next step in modelling might extend to copper oxidation with Monte Carlo simulation of half-cell Cu oxidation reactions (for an anodic inhibitor) for various copper sites with adsorbed molecules as well as for first, second and third nearest neighbours [7]. This will further enhance understanding of the role(s) of inhibiting ions and in order to move beyond the notion that strong adsorption is desired followed by the subsequent assumption that sites of adsorption are blocked while unblocked sites corrode as if no inhibitor were in the system at all; with each site behaving independently.

These studies are a significant advance over semi-empirical quantum chemistry approaches where the physicochemical properties of molecules in isolation are correlated with corrosion inhibition [19]. Relationships are sought between a number of molecular properties such as orbital energies, dipole moment, charge density, and other aspects [19]. This has been called the quantitative structure activity relationship or QSAR approach. For instance, in this approach the energies of the highest and lowest density occupied states of the inhibiting molecule in isolation are often used as a metric. A correlation between inferred coverage due to these attributes and corrosion inhibition is often attempted.

Finally, not only must the quantification of the various types and strengths of interactions of molecules with surfaces be considered. The modelling of dissolution rate with proximate inhibitor molecules is a good starting point. However, many other aspects such as electrolyte flow rate, colloidal properties and multi-layering corrosion scales, wetting, biocide capability, and inhibiting films must be considered to provide a comprehensive view of how corrosion inhibitors operate [18].

4 Corrosion Science and Engineering

Complex dissolution processes experienced during corrosion of commercial and model alloys in complex environments were discussed. Mirroring the technological needs of the field, some papers “took on this issue” in all of its complexity [14, 20, 21]. Specialized *in-situ* mapping techniques, combination of complementary techniques and/or control of single corrosion sites were some of the different strategies used to address this [20-23]. A recent advance includes the plethora of scanning probe techniques (SPTs) available for enhanced spatial resolution of corrosion in real time. Moreover, *operando* optical microscopy with long focal length microscopes remains of great utility [20, 21, 23, 24]. New approaches such as the scanning electrochemical microscope (SECM) and scanning vibrating electrode technique (SVET) also were used in combination with more traditional DC electrochemistry methods. A continued challenge is the inability to acquire simultaneous data on multiple aspects of alloy corrosion at the same time and over the same length scale such as chemistry changes at surfaces while monitoring element-by-element dissolution and filming. Assessment of all types of anodic and cathodic reactions differentiated by ½ cell type with high spatial resolution continues to be highly desirable capability needed to unravel complex alloy dissolution.

4.1 Localized Corrosion and Complex Alloy Dissolution

Spatially confined corrosion phenomena (e.g., pitting), which can lead to rapid failure of otherwise corrosion resistant substrates were addressed. [1] Studies aiming to understand at the nanoscale the combined influences of substrate microstructure/geometry, and fluid chemistry on complex alloy and local corrosion initiation/progression were presented [1]. One of the enduring themes was how complex alloy corrosion remains. Major, minor, and trace alloying elements impart a significant impact on corrosion and certain elements or phases often interact critically with specific solution chemistries[14, 20-25].

Anodic polarization of light alloys such as magnesium and aluminium can exhibit extraordinary rates of the hydrogen evolution reaction (HER) often observed in anodic areas. [26] This observation is counter to basic mixed potential theory which assumes that the HER rate decreases as applied potentials become more anodic and the hydrogen over potential is lowered. Hydrogen production reaches a minimum near open circuit conditions and is often intensified at more positive applied anodic currents with increasing metal dissolution rates. In the Mg corrosion literature this has been called the negative difference effect [26]. Anodically enhanced hydrogen evolution (HE) has been observed in many alloy systems and modelled based on hydrolytic acidification and ohmic drop in pits and cracks [27]. However, the opening lecture posited that at high anodic reaction rates, hydrogen production may become “super-catalysed” as verified by hydrogen gas collection by mechanisms under current debate [26]. The notion is that the exchange current density for HER increases during anodic polarization to a much great extent than the anodic overpotential; thereby offsetting a decrease in hydrogen overpotential. The concept could apply to a number of light metals which oxidize during open circuit corrosion and anodic at potentials far below reversible hydrogen. The various contributions to the effect (for instance the contributions from hydrolytic acidification and ohmic voltage drop [27], impurities [28, 29], films, versus special sites which may affect the activation barrier of facile HE have not been clarified. Moreover, the study highlights some of the difficulty of gaining corrosion information from DC electrochemical methods which only measure net current and are not spatially resolved. Ramifications towards hydrogen embrittlement of Al were discussed [26,30-34]. Hydrogen embrittlement during freely corroding and anodic polarization in occluded sites is certainly observed during light alloy corrosion as well as steel and local hydrogen production has been shown to play a strong role [27, 32, 35, 36]. High hydrogen levels local to anodically polarized crack tips are observed in numerous systems such as Al and Ti [32, 34, 36, 37]. Additional study of hydrogen interactions with surfaces and precise effects of surface atom defects and coordination chemistry on reduction and oxidation processes are clearly warranted[3, 7, 8, 38].

Mg dissolution was discussed further, considering the effects of various trace levels of iron on localized corrosion morphology [23]. The theme of complex corrosion patterns was covered. For instance, the morphology of Mg corrosion changes with various Fe impurity levels in solutions of various ionic strength (conductivity) [23]. Here anodically induced cathodic enrichment was observed and the formation of dark areas forming various corrosion patterns[29, 39]. It was rationalized that these were regulated by Cl^- and Fe content [23].

Complex interaction between thiosulfate and halides with three distinctly different alloys illustrates how radically different pitting morphologies may result from differences in alloy chemistry, mutual electro-migration of differently charged ions and the presence of reacting species. The oxide breakdown process was short circuited or otherwise circumvented by scratching anodes. Studies were conducted in complex solutions containing several anions, some which attack the metal and support hydrolytic acidification, as well as others which react to form very detrimental species such as sulphur [14]. The localized (e.g., pitting corrosion process) involved propagation of individual pits interacting dynamically with the chemistry of the solution and each other. Strong potential, solution chemistry and alloy tendencies were observed pointing to the complexity of the issue. For instance a lack of alloyed Mo contributed to pitting at low potentials in sulphate. The debate over the relative roles and contributions of alloyed Mo in connection with the passive film versus the propagation and stabilization stage of pitting was continued. The morphologies of both local and multiphase alloy attack were also discussed. Scanning probe techniques (SPTs) of various types have come of age in studying corrosion patterns on microstructural complex alloys. Methods discussed included SVET, SECM, and a novel shear force mounted scanning micro-capillary method[20, 21, 23]. There is a current focus within complex alloy corrosion research on light alloys such as micro-galvanically coupled Mg alloy ZEK100, zinc magnesium aluminium alloys, (ZMA), precipitation age hardened aluminium, and emerging steels [20, 21, 23]. Stainless steel and nickel based alloys continue to be of interest given their immense technological importance. [14, 22, 24] Future directions likely include high entropy alloys, 2-D materials, and others produced by high energy processes far from equilibrium.

Complicated patterns of corrosion develop as a function of alloy, solution chemistry, and electrolyte geometry (i.e., droplets) and these patterns are controlled by a variety of factors such as active corrosion versus passive breakdown [24], electromigration of differently charge ions and anion ratios [14], alloy microstructure including anodic and cathodic phases [20, 21], proximate cathodic reactions, and cathodic limited growth versus ohmically limited growth [23]. In another strategy, a single isolated pit was produced and controlled using a capillary drop method [22]. Critical concentrations, critical ratios of chemical species and critical depths were all envisioned to produce "windows of susceptibility" versus "kinetic immunity" [14, 22, 24].

In summary, the SPTs provided a strategy for operando studies and dealt with the incredible complexity of alloy dissolution. The dissolution morphologies observed are infrequently on the length scale of the microstructural features in the alloy illustrating the complexity of the issue. Progress to elucidate complex alloy corrosion continues fuelled often by (i) alloy "du jour" technological needs, and (ii) the adaptation of new or emerging techniques often developed in other fields such as biology, chemistry, surface science and applied electrochemistry.

4.2 Modelling of Defined Aspects of Corrosion Processes

Just as fundamental parameters and the details of specific unit processes must be understood, these processes must be assembled in meaningful ways to provide a more complete view of complex corrosion phenomena. Several papers were presented which modelled defined aspects of corrosion processes. Further progress will likely accelerate in this area [18, 40, 41]. Once models can be developed which can capture as many unit processes as necessary to faithfully describe a corrosion process then they can be exercised over a broad range of plausible input conditions to gain insight on the importance of variables to various outcomes, identify potential regulating factors during corrosion and even guide more focused experiments directed towards deeper insight. This differs from Edisonian experimental approaches where high throughput methods are used to rapidly map out response surfaces for corrosion processes under a broad range of conditions without much fundamental insight. High throughput methods are a worthy starting point for corrosion discovery when there is no model and little idea as to what is important. However, this approach can be improved upon as a corrosion process becomes understood well enough to model.

A mechanistic model of the oxide growth and dissolution of Cr-containing alloys was one example [40]. The model considered both electrochemical and chemical reactions at the metal/oxide and oxide solution interfaces. These included metal oxidation, oxide growth, and oxide dissolution. Charge as well as mass balances were maintained. Selected unit processes that operate together to regulate film formation were collected and dealt with together in one model [40]. The cation flux was quantified, while charge as well as mass balances were imposed. Noteworthy was that the metal cation flux at the metal/oxide interface must equal the sum of oxide growth and oxide dissolution rates at the oxide/solution interface. The effects of temperature, environmental chemistry and oxide thickness were all incorporated. Time dependent behaviour was predicted for pure iron, Co-Cr and Fe-Ni-Cr alloys. In another example, the synergistic influences of hydrogen peroxide and H_2 on simulated spent nuclear fuel corrosion were considered in a model framework where variations in corrosion potential, redox conditions, HCO_3^-/CO_3^{2-} and convective conditions all mediated U oxidation by H_2O_2 that could be reversed by H_2 [41]. In this way, these various factors were all captured and were shown to operate in concert to govern spent fuel corrosion controlled by the chemical dissolution rate of the U(VI) layer. For instance, HCO_3^-/CO_3^{2-} could prevent formation of insulating U(VI) layers.

The need for multi-physics, multi-domain type approaches that collect a wide range of different processes and incorporate them all in a multi-length scale, multi-time scale model that captures the physical, chemical and electrochemical processes necessary to describe corrosion was clear [18]. Finally, risk assessment was mentioned as a capstone to the models [18]. The future of corrosion modelling will likely involve collection of the fundamental information discussed above, elucidation of the unit processes, plausible model frameworks, and then multi-scale models that can accurately meet the challenge of accurately forecasting corrosion.

4.3 Corrosion Control and Mitigation by Coatings, Pigments, and Inhibitors

The largest practical area of corrosion control is by coatings, paints, and corrosion inhibitors. Nanoscale understanding of corrosion control methods was emphasized [1]. In particular, situations were addressed where altered surface chemistry, often of a multi-layered nature, played a key role in corrosion mitigation. Topics of discussion centred on those critical to obtaining mechanistic insight into corrosion control, including substrate bonding, structure/morphology, interfacial transport, and degradation mechanisms of coatings and treatments [1]. The future of corrosion control likely involves multi-functional solutions guided by the science behind individual steps in the coating degradation process.

Some topics of focus included replacement pigments for chromate, novel graphene and electro-reactive coatings, water uptake in intact organic coatings and film forming or molecular adsorbing inhibitors [16-18, 25, 42-45]. The benefits of atomistic scale observation were evident from the study of adsorbing inhibitors in the case of dealloying. Here, adsorbing inhibitors which formed a film and limited surface diffusion were effective towards limiting dealloying from solid solution alloys where one element was displaced far from its equilibrium oxidation potential. However, the inhibitor offered no long range protection since absence of the inhibitor on metal sites led to rapid dealloying.

Concerning, traditional engineered coatings, the behaviour of “intact coatings” which are a barrier to corrosion is of great importance. Here, degradation is driven by electrolyte uptake, transport and the development of microscopic defects and fast transport pathways in polymer coatings. Another important focus is corrosion control at “macro defects” in coatings[25,44]. In the former, long term organic coating failure was envisioned to occur through the development of ionic water channels; moisture sorption, and hydrogen bonding between the coating and water [44]. Nanoscale softening occurred as the coatings became plasticized. Increased wetting and a drop in the glass transition temperature both occurred as well. In the case of an artificial defect such as a physical scratch exposing bare metal, the challenge is to protect the bare area enabled by the functional response of the adjacent pigmented coating. Lithium bearing salts were incorporated in the coating as a leachable pigment in one example. Focus was on the ability of the pigment to supply Li forming compounds to create a deposit or conversion coating over the artificial scratch which exposed the engineering alloy substrate alloy (2024 or another other precipitation age hardened high strength Al alloy). The morphology and chemical nature of the scale formed over the scratch was characterized. It is interesting to consider these two contrasting areas of study; one focused on the bare metal and the adjacent pigmented polymer and the ability to release, transport and form a protective layer over the bare scratch [25, 44]. The other focused on the details of polymer degradation with respect to the “intact coating”. Radically different aspects of time dependent polymer degradation, as well as storage/release processes are at play and many of properties of interest differ from those typical of corrosion science. Clearly, both aspects must be studied in order to advance the understanding of coatings for corrosion control. There is the need for tools to observe and characterize both processes [44]. Corrosion science in this area could be furthered by capturing inhibitor release, transport and deposition in developing models, as well as to understand the attributes of so called smart coatings for successful protection of coating defects. Fortunately recent advances in continuum scale computational modelling can now be incorporated to address the efficacy of a pigment; for instance, regarding its ability to release and deliver the needed chemicals to protect a scratch[46-52]. Computational design of “scratch” protection schemes for coating defects is now possible including electrochemical scratch protection.[53]. This type of approach could be used to study corrosion inhibition at coating defects using all kinds of strategies such as by partially soluble pigments or electroactive coatings where release might be triggered in response to environmental stimulation [47, 52, 54-59].

Novel coatings are also a key part of future corrosion control strategies[42,43]. A conducting polymer with good adhesion was discussed. A closely related challenge is interface engineering to optimize adhesion and corrosion protection by producing favourable interface chemistries. The behaviour of graphene as a single molecular layer which is impermeable, transparent, flexible, and stable provides an interesting contrast. The impenetrable graphene layer is noteworthy but the edge exposed regions and subsequent lateral transport under the graphene over layer is an important area of focus as it presents a weakness or potential flaw in the successful utilization of this mitigation strategy [43]. Graphene may not ultimately provide the answer to corrosion control, but is symbolic of the novel thinking that must be a part of an “all of the above” approach to corrosion control. It is also clear that no one aspect – neither the intact coating nor the defect can be considered in isolation. New technologies such as graphene and a mix of traditional methods and approaches must all be considered to improve corrosion. It was clear from these studies that, as in the case of passive films, the combination of detailed morphological, chemical and electrochemical information, preferably in-situ will be of immense value towards future progress. In terms of modelling, a multi-scale approach must also be considered using first principle tools, continuum scale models combined with consideration of multiple physical phenomena. Since coating like other materials contain a variable population of defects such modelling should include uncertainty analysis [18].

Conclusions

Recent advances in characterization tools, computational capabilities and theory have created opportunities for advancement in understanding of solid/fluid interfaces at the nanoscale in corroding systems. The Faraday Discussion on Corrosion Chemistry highlighted some of the current and future needs, gaps and opportunities in the field of corrosion science. Themes could be organized into several hierarchal categories that provide a framework for inspiring further progress in corrosion science. These include foundational areas such as the need and opportunity to access fundamental physical and chemical data to further progress in thermodynamic and kinetic modelling, further improvements and new ways to understand unit processes that govern corrosion at the nanoscale such as better understanding and control of scales, films and oxides, fluid-surface and molecular-surface interactions, as well as selected topics in corrosion science and engineering. Challenges were identified in each of these theme areas. Corrosion involves multiple processes, occurring at different length and time scales; these in combination and in certain hierarchal relations with one another ultimately govern engineering scale behaviour. Multiple simultaneous tools to characterise corrosion at a sub-micrometre scale and on an in-situ or operando basis are required. At the same time information is necessary on a larger length scale that factors in smaller length scale defects and features. More comprehensive and complete analysis of corrosion processes by modelling requires multi-physics based approaches which must consider these many processes – often together. The question arises, is the corrosion field making progress? The answer is yes, but progress is fragmented for a wide variety of reasons. Scientific advancement often occurs by piecing together isolated pockets of progress. Researchers are encouraged to find value in many of the studies discussed herein even if they are in an environment or on a different material that may not seem to be of immediate interest. Further advances in operando characterizations and computational modelling will enhance progress in the field, especially if coupling across length and time scales incorporating the various phenomena encountered in corrosion can be achieved and successful multi-scale approaches are found.

Acknowledgements

Support from the National Science Foundation DMR-1309999 under the direction of Dr. Gary Shiflet is gratefully acknowledged. This work was also partially supported by an ONR MURI Program under the direction of Dr. David Shifler titled "Understanding Atomic Scale Structure in Four Dimensions to Design and Control Corrosion Resistant Alloys on Grant Number N00014-14-1-0675.

References

1. R. Lindsey, Corrosion Chemistry Faraday Discussion Web Site, (accessed April, 2015, 2015).
2. M. Todorova and J. Neugebauer, *Faraday Discussions*, 2015.
3. J. K. Norskov, T. Bligaard, B. Hvolbaek, F. Abild-Pedersen, I. Chorkendorff and C. H. Christensen, *Chem Soc Rev*, 2008, 37, 2163-2171.
4. D. Kramer, Y. Wang and J. A. Wharton, *Faraday Discussions*, 2015.
5. H. A. Hansen, J. Rossmeisl and J. K. Norskov, *Phys. Chem. Chem. Phys.*, 2008, 10, 3722-3730.
6. S. R. Taylor, G. J. Shiflet, J. R. Scully, R. G. Buchheit, W. J. VanOoij, K. Sieradzki, R. E. Diaz, C. J. Brinker and A. L. Moran, *Corros Rev*, 2007, 25, 491-522.
7. C. D. Taylor, M. Neurock and J. R. Scully, *Journal of the Electrochemical Society*, 2011, 158, F36-F44.
8. D. J. Horton, A. W. Zhu, J. R. Scully and M. Neurock, *Mrs Commun*, 2014, 4, 113-119.
9. J. Lutzenkirchen, F. Heberling, F. Supljika, T. Preocanin, N. Kallay, F. Johann, L. Weisser and P. Eng, *Faraday Discussions*, 2015.
10. O. Karslioglu, S. Nemsak, I. Zegkinoglou, A. Shavorskiy, M. Hartl, F. Salmassi, E. Gullikson, M.-L. Ng, C. Rameshan, B. Rude, D. Bianculli, A. Cordones-Hahn, S. Axnanda, E. Crumlin, P. N. Ross, C. M. Schneider, Z. Hussain, Z. Liu, C. S. Fadley and H. Bluhm, *Faraday Discussions*, 2015.
11. B. Ingham, M. Ko, N. Laycock, N. M. Kirby and D. E. Williams, *Faraday Discussions*, 2015.
12. V. Maurice, H. Peng, L. H. Klein, A. Seyeux, S. Zanna and P. Marcus, *Faraday Discussions*, 2015.
13. R. Springell, S. Rennie, L. Costelle, J. Darnbrough, C. A. Stitt, E. Cocklin, C. Lucas, R. Burrows, H. E. Sims, D. Wermeille, J. Rawle, C. Nicklin, W. Nuttall, T. Scott and G. Lander, *Faraday Discussions*, 2015.
14. W. Zhang, A. G. Carcea and R. C. Newman, *Faraday Discussions*, 2015.
15. V. Wagener, A.-S. Faltz, M. S. Killian, P. Schmuki and S. Virtanen, *Faraday Discussions*, 2015.
16. C. Gattinoni and A. Michaelides, *Faraday Discussions*, 2015.
17. A. Kokalj, *Faraday Discussions*, 2015.
18. C. Taylor, A. Chandra, J. Vera and N. Sridhar, *Faraday Discussions*, 2015.
19. N. Khalil, *Electrochim Acta*, 2003, 48, 2635-2640.
20. P. Dauphin-Ducharme, W. J. Binns, M. E. Snowden, D. W. Shoesmith and J. Mauzeroll, *Faraday Discussions*, 2015.
21. J. Sullivan, N. Cooze, C. Gallagher, T. Lewis, T. Prosek and D. Thierry, *Faraday Discussions*, 2015.
22. S. Heurtault, R. Robin, F. Rouillard and V. Vivier, *Faraday Discussions*, 2015.
23. G. Williams, N. Birbilis and N. McMurray, *Faraday Discussions*, 2015.
24. T. Rayment, S. R. Street, N. Mi, A. J. M. C. Cook, H. B. Mohammed-Ali, L. Guo and A. Davenport, *Faraday Discussions*, 2015.
25. P. Visser, Y. Lui, X. Zhou, T. Hashimoto, G. Thompson, S. Lyon, L. G. J. van der Ven, A. J. M. C. Mol and H. Terryn, *Faraday Discussions*, 2015.
26. G. S. Frankel, S. Fajardo and B. M. Lynch, *Faraday Discussions*, 2015, Royal Society of Chemsitry.
27. B. A. Kehler and J. R. Scully, *Corrosion*, 2008, 64, 465-477.
28. N. Birbilis, A. D. King, S. Thomas, G. S. Frankel and J. R. Scully, *Electrochim Acta*, 2014, 132, 277-283.
29. T. Cain, S. Madden, N. Birbilis and J. Scully, *Journal of the Electrochemical Society*, 2015, 162, C228-C237.
30. J. H. Ai, M. L. C. Lim and J. R. Scully, *Corrosion*, 2013, 69, 1225-1239.
31. J. H. Ai and J. R. Scully, *Corrosion*, 2013, 69, 752-767.
32. G. A. Young and J. R. Scully, *Metall Mater Trans A*, 2002, 33, 1167-+.
33. J. R. Scully, G. A. Young and S. W. Smith, eds., *Hydrogen solubility, diffusion and trapping in high purity aluminum and selected Al-base alloys, Gaseous Hydrogen Embrittlement of Materials in Energy Technologies, Vol 1*, 2012.
34. G. A. Young and J. R. Scully, *Acta Mater*, 1998, 46, 6337-6349.
35. D. G. Kolman, M. A. Gaudett and J. R. Scully, *Journal of the Electrochemical Society*, 1998, 145, 1829-1840.
36. D. G. Kolman and J. R. Scully, *Metall Mater Trans A*, 1997, 28, 2645-2656.
37. D. G. Kolman and J. R. Scully, *Corrosion Science*, 2000, 42, 1863-1879.
38. K. S. Williams, J. P. Labukas, V. Rodriguez-Santiago and J. W. Andzelm, *Corrosion*, 2015, 71, 209-223.
39. L. G. Bland, A. D. King, N. Birbilis and J. R. Scully, *Corrosion*, 2015, 71, 128-145.
40. M. Momeni and J. C. Wren, *Faraday Discussions*, 2015.
41. M. Razdan and D. W. Shoesmith, *Faraday Discussions*, 2015.
42. Y. Konno, E. Tsuji, Y. Aoki, T. Ohtsuka and H. Habazaki, *Faraday Discussions*, 2015.

43. L. Kyhl, S. F. Nielsen, A. G. Cabo, A. Cassidy, J. A. Miwa and L. Hornekaer, *Faraday Discussions*, 2014.
44. S. Morsch, S. Lyon, P. Greensmith, D. Smith and S. R. Gibbon, *Faraday Discussions*, 2015.
45. B. R. Shrestha, A. Bashir, G. N. Ankah, M. Valtiner and F. U. Renner, *Faraday Discussions*, 2015.
46. M. A. Jakab, F. Presuel-Moreno and J. R. Scully, *Corrosion*, 2005, 61, 246-263.
47. M. A. Jakab and J. R. Scully, *Nat. Mater.*, 2005, 4, 667-670.
48. M. A. Jakab and J. R. Scully, *Corrosion*, 2008, 64, 198-209.
49. F. Presuel-Moreno, M. A. Jakab, N. Tailleart, M. Goldman and J. R. Scully, *Mater. Today*, 2008, 11, 14-23.
50. F. J. Presuel-Moreno, M. E. Goldman, R. G. Kelly and J. R. Scully, *Journal of the Electrochemical Society*, 2005, 152, B302-B310.
51. F. J. Presuel-Moreno, H. Wang, M. A. Jakab, R. G. Kelly and J. R. Scully, *Journal of the Electrochemical Society*, 2006, 153, B486-B498.
52. J. R. Scully, F. Presuel-Moreno, M. Goldman, R. G. Kelly and N. Tailleart, *Corrosion*, 2008, 64, 210-229.
53. A. King, J. Lee and J. Scully, *Journal of the Electrochemical Society*, 2015, 162, C12-C23.
54. M. Kendig and M. Hon, *Corrosion*, 2004, 60, 1024-1030.
55. M. Kendig, M. Hon and L. Warren, *Prog Org Coat*, 2003, 47, 183-189.
56. M. Kendig and P. Kinlen, *Journal of the Electrochemical Society*, 2007, 154, C195-C201.
57. A. D. King, B. Kannan and J. R. Scully, *Corrosion*, 2014, 70, 536-557.
58. A. D. King, B. Kannan and J. R. Scully, *Corrosion*, 2014, 70, 512-535.
59. A. D. King and J. R. Scully, *Corrosion*, 2011, 67.